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DEVELOPMENT OF A HIGH EFFICIENCY

THIN SILICON SOLAR CELL

JPL Contract No. 954290

March, 1976

Second Quarterly Report

Report No. SX/105/2Q

by

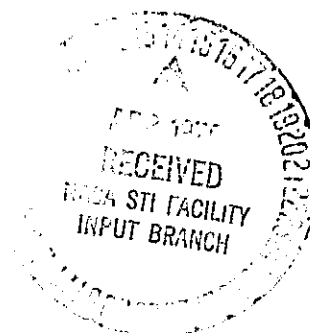
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TECHNICAL CONTENT STATEMENT

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I. ABSTRACT

Progress in this contractual quarter was concentrated on mapping the back-surface internal reflectance as a function of alloying conditions, evaluation of ultra-fine gridline improvements, anti-reflection coating optimization, stability testing and fabrication of a larger number of sample cells.

It was found that optimum internal optical reflection at the back alloy surface occurs for alloy temperatures too high for maintenance of good fill factors and blue response. However, in the useful temperature range, the reflectance is still near 60%.

The new gridline pattern with 5 micron linewidths resulted in a 1.3% improvement in short-circuit current compared to the previous pattern with 13 micron linewidths.

The anti-reflection coating optimization task under this contract was completed in this quarter. High-index, high-transmittance, extremely adherent coatings were routinely achieved.

The scheduled stability tests were performed during the quarter and produced no measurable changes in the properties of the cells.

One hundred cells of various thicknesses are being submitted to JPL as the second sample group.

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III. SUMMARY

The purpose of this investigation is to improve process parameters which influence high-efficiency, thin silicon solar cell performance. In the course of this contractual effort, a significant number of solar cells nominally 4 cm^2 will be fabricated and analyzed, of which 500 are to be submitted to JPL for evaluation. This investigation is both experimental and theoretical in nature, as feedback to changes in experimental process parameters requires analysis of cell performance parameters and comparison to modelled properties for assessment of probable underlying physical phenomena which can be altered experimentally.

In this quarter, the internal optical reflection at the alloyed back surface was evaluated as a function of crystal orientation and alloying temperature. It was found that a [100] aluminum-alloyed silicon surface generally results in essentially the same reflection as a similarly prepared [111] surface. Also, while the alloy-silicon interface usually produces approximately 60% reflection if the alloy is performed at temperatures which do not greatly perturb the phosphorus diffusion, alloying at temperatures in excess of 900°C produces an abrupt increase in interface reflection to approximately 80%. However, at such a high alloying temperature, the fill factor and blue response are badly degraded, although the red response benefits from the reflection.

During this quarter, the new masks for the reduced-linewidth gridline pattern (discussed in the previous quarterly report) were received and employed in cell fabrication. Excellent cell

characteristics were obtained, and the increase in I_{sc} due to the reduction in shadowing from the previous pattern was 1.3%.

Studies of conditions for applying tantalum oxide as an anti-reflective coating have led to the conclusion that the least-absorbing, highest-index films are achieved by employing an evaporant source of oxide that was previously melted in vacuo. Freshly prepared powder sources or oxygen back pressures during evaporation result in inferior film characteristics.

Cells were subjected to 150°C thermal soaks for 48 hours, followed by thermal cycling from 100°C to -196°C. No deterioration in either electrical or mechanical characteristics was found for any cell tested.

As required, a sample of 100 experimental 2cm x 2cm cells, which were fabricated during the quarter, were forwarded to JPL for evaluation.

IV. TECHNICAL DISCUSSION

A. Internal Reflection

The purpose of this task is two-fold: first, to analyze the optical properties of the back interface for its effect on the longer wavelength end of the spectrum and, second, to attempt maximizing reflection at that interface for increasing the red response of thin solar cells.

Numerous samples were prepared on both [100] and [111] silicon slices for alloying over a range of temperatures and subsequent measurement of the internal reflection at the resulting interface. As in cell fabrication, aluminum was evaporated onto the silicon surface and then alloyed into the silicon for a given time at a particular temperature. Separate samples were used for each time and temperature.

The optical measurements were performed with the Beckman DK-2A spectrophotometer and Gier-Dunkle integrating sphere in the Solarex laboratories. The measured quantity was the net reflection at wavelengths slightly longer than the silicon absorption band. In that range the silicon is a non-absorbing window and the reflection measured is a result of both the front-surface air/silicon and the rear silicon/alloy interfaces. The reflection at the rear interface can be calculated from the measured net reflection when the properties of the front-surface interface are known. Experimentally, the front silicon surface was smooth and cleaned in a mild hydrofluoric acid solution to produce a controlled known interface prior to measurement.

The net reflection from a series of two interfaces is:

$$R = \frac{R_1 + R_2}{1 + R_1 R_2}$$

where R_1 is the reflectance of the first interface in the light path and R_2 is that of the second interface encountered in the light path. In this case, R_1 is due to the differing refractive indices of air and silicon at a wavelength of 1.3 microns. It is:

$$R_1 = \left(\frac{n_{\text{Si}} - n_{\text{air}}}{n_{\text{Si}} + n_{\text{air}}} \right)^2 = 0.31$$

The value of R_2 can thus be calculated from measured net reflection by inserting 0.31 for R_1 in the first expression above, as:

$$R_2 = \frac{R - 0.31}{1 - 0.31R}$$

Typical plots of net reflection as a function of wavelength is shown in Figure 1. Note that the reflection becomes essentially wavelength independent for wavelengths beyond 1.3 microns.

Calculated values for the silicon/alloy interface reflectance derived from measurements are shown in Figure 2 for [100] surfaces and in Figure 3 for [111] surfaces. Before alloy, R_2 was found to be in the immediate neighborhood of 0.8. After alloying, the interface reflectance decreases; most likely the mirror darkening is due to absorption in the recrystallized layer at the interface. Below the temperature of the silicon-aluminum eutectic, the sintering effect produces little disturbance of the mirror properties. However, from the eutectic up to 850°C there is a drop in reflectance to the range of 0.5 to 0.6, with a good deal of scatter from sample to sample.

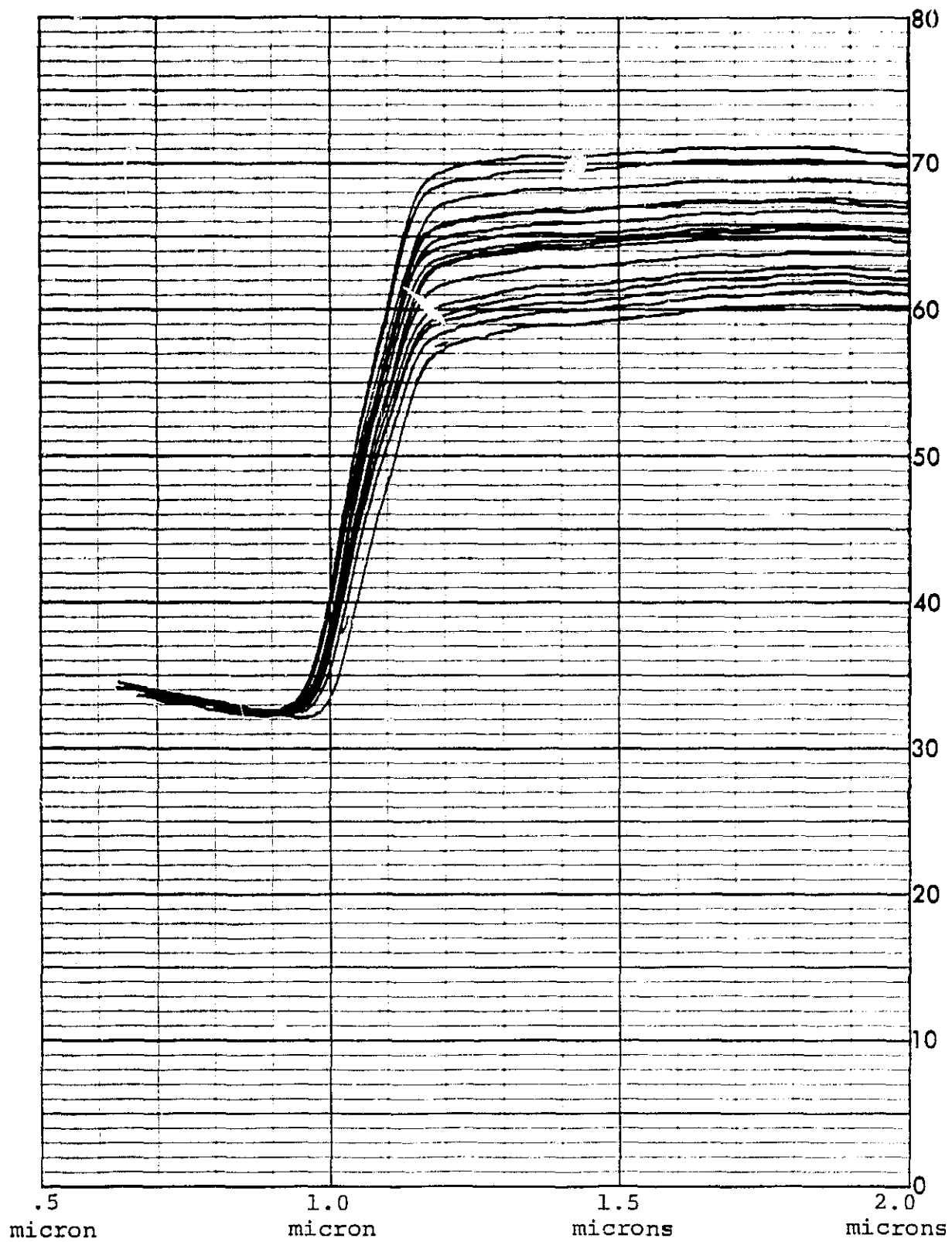


FIGURE 1. NET REFLECTION AS A FUNCTION OF WAVELENGTH

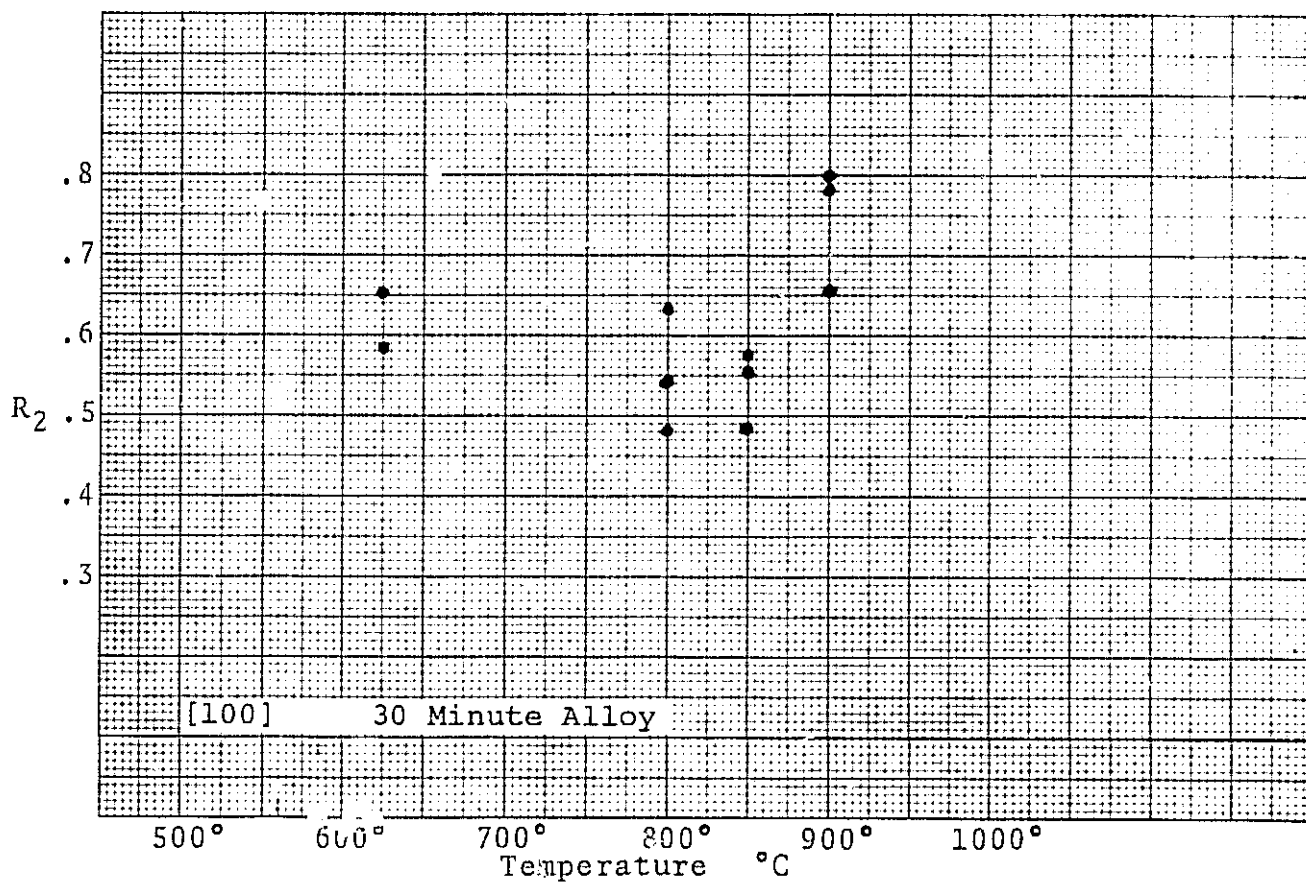
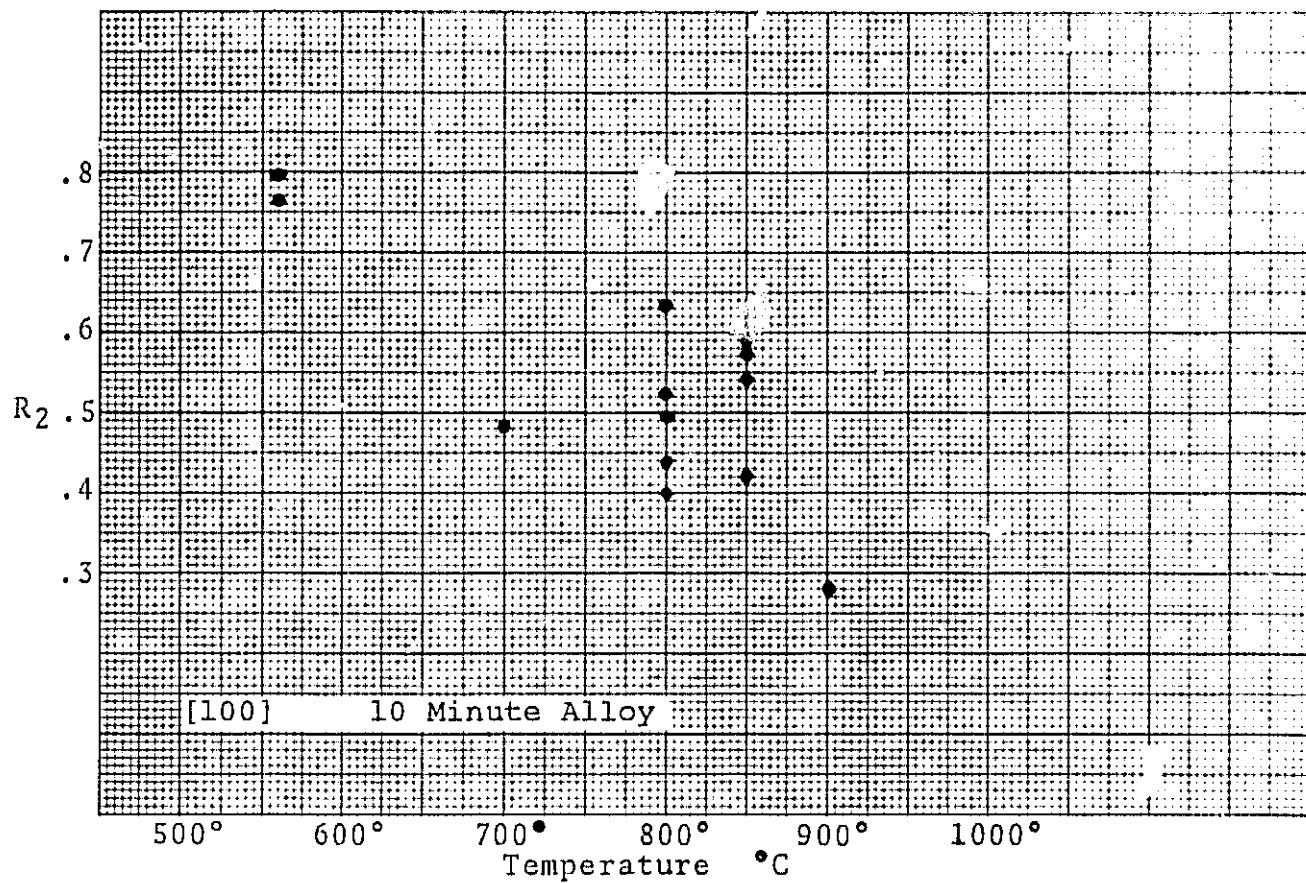


FIGURE 2. REFLECTION OF Si Al INTERFACE (R_2) VS. ALLOY TEMPERATURE

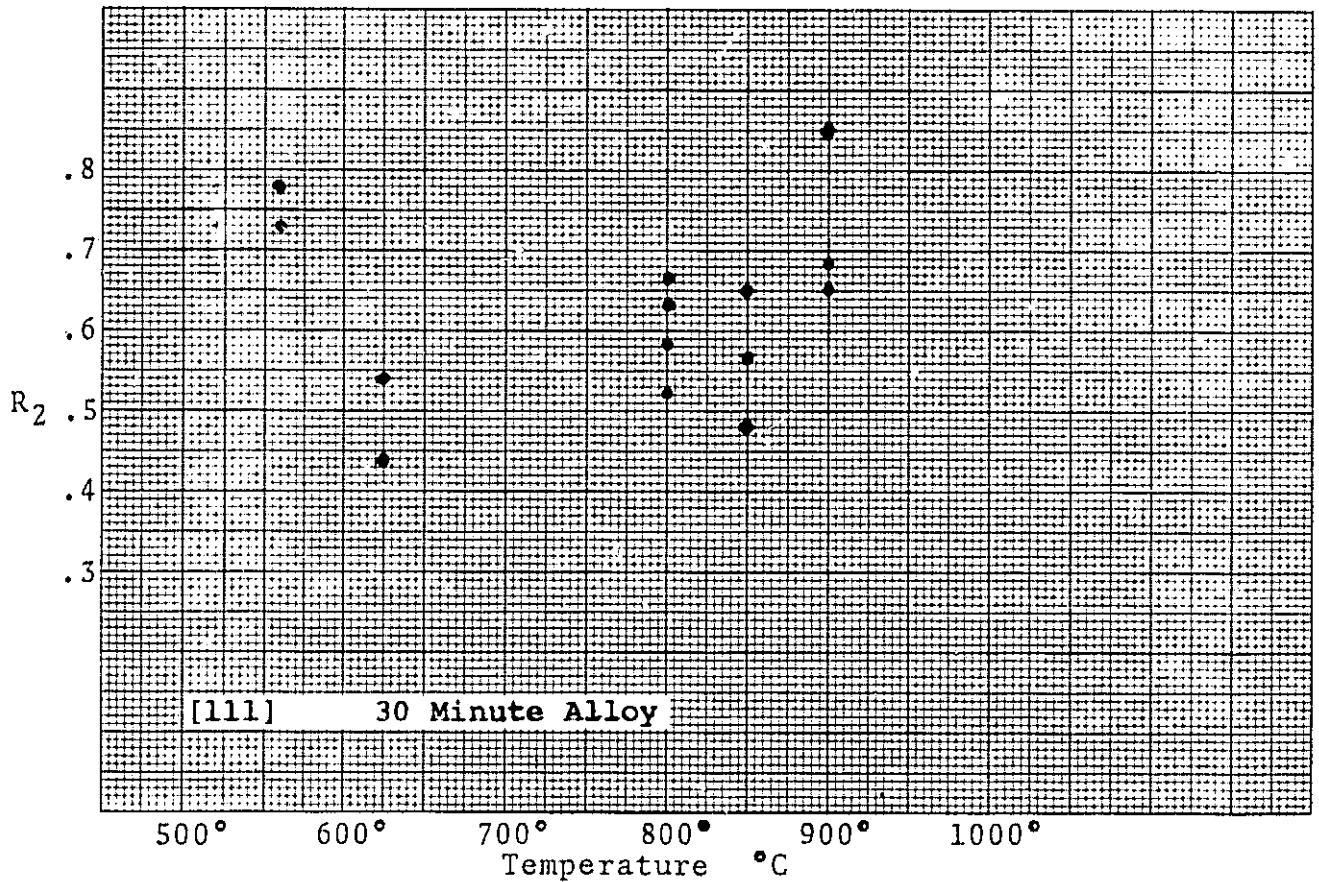
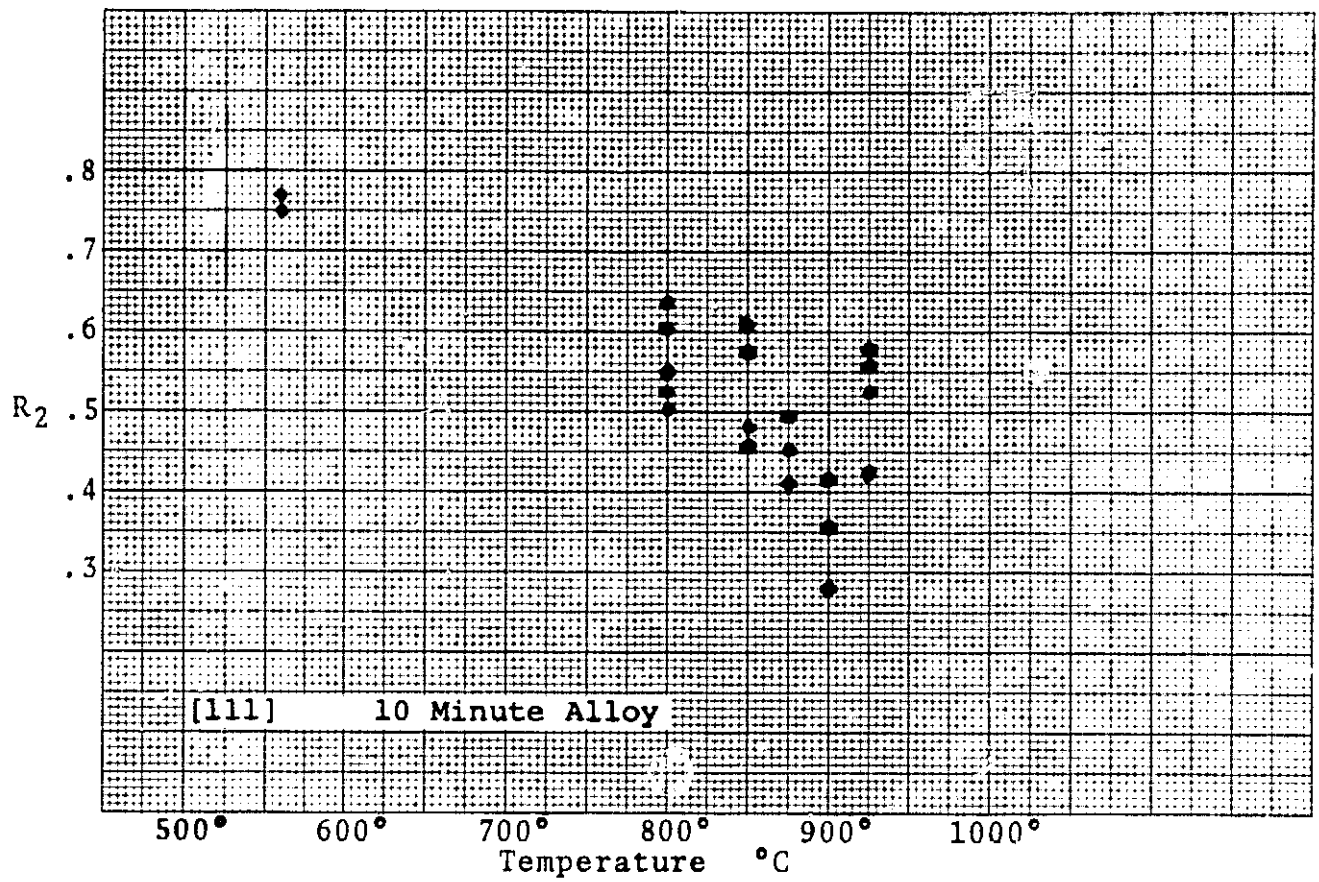


FIGURE 3. REFLECTION OF Si Al INTERFACE (R₂) VS. ALLOY TEMPERATURE

For sufficiently long alloying times at temperatures of 900°C or higher, an increased reflectance reappears, although still with considerable scatter from sample to sample.

The main conclusion to be drawn is that the reflectance of the silicon/aluminum interface is high only for treatment at temperatures below the eutectic or long alloying above optimum phosphorus diffusion temperatures. Otherwise, a reflectance in the neighborhood of 50 - 60% will result.

These reflectance experiments indicate that:

1. The scatter in cell performance as a function of 650°C-850°C alloy temperature reported previously was probably due to the scatter in reflectance values and their effect on the red component of the short-circuit currents.

2. Utilization of high internal reflectance would require a process with avoidance of the silicon-aluminum eutectic after aluminum application or other different process techniques to utilize a high (900°C +) temperature alloy.

For verification of the effect of high optical reflectance at the silicon/alloy interface, a small quantity of cells were fabricated with a 925°C alloy. Employing such a high alloy temperature ruined the fill factors and open-circuit voltages, but the red component of the short-circuit current increased by over 10mA for the 2cm x 2cm cells, which were 200 microns thick.

B. Gridline Optimization

During the previous quarter, a new gridline design was generated, to generally narrow the finest linewidths employed to the practical limit of approximately 5 microns. Summing sub-busses were also reduced in linewidth, but the 1mm x 2mm contact areas were retained as previously.

During this quarter, the new-design masks were received and employed in processing hundreds of cells. Small comparison lots processed with half of the cells receiving the old pattern and half with the new design demonstrated an improvement in short-circuit current of approximately 1.3%. The linewidth reduction (described in detail in the previous quarterly report) from 13 microns to 5 microns in the finest lines should have produced a 0.4% reduction in shadowing and the sub-buss width reduction approximately 1.0%, the sum of which agrees fairly well with the observed improvement. Figure 4 shows typical I-V characteristics for co-processed 2cm x 2cm cells using the two patterns.

C. Anti-reflection Coating

During this quarter, efforts were also directed to studying tantalum oxide anti-reflective coating on silicon. It was found that regardless of the deposition technique employed, all films were extremely adherent and the main changes incurred related to net reflectance and refractive index.

The experiments performed varied the source material condition, evaporation rate, oxygen back pressure and post-deposition treatment.

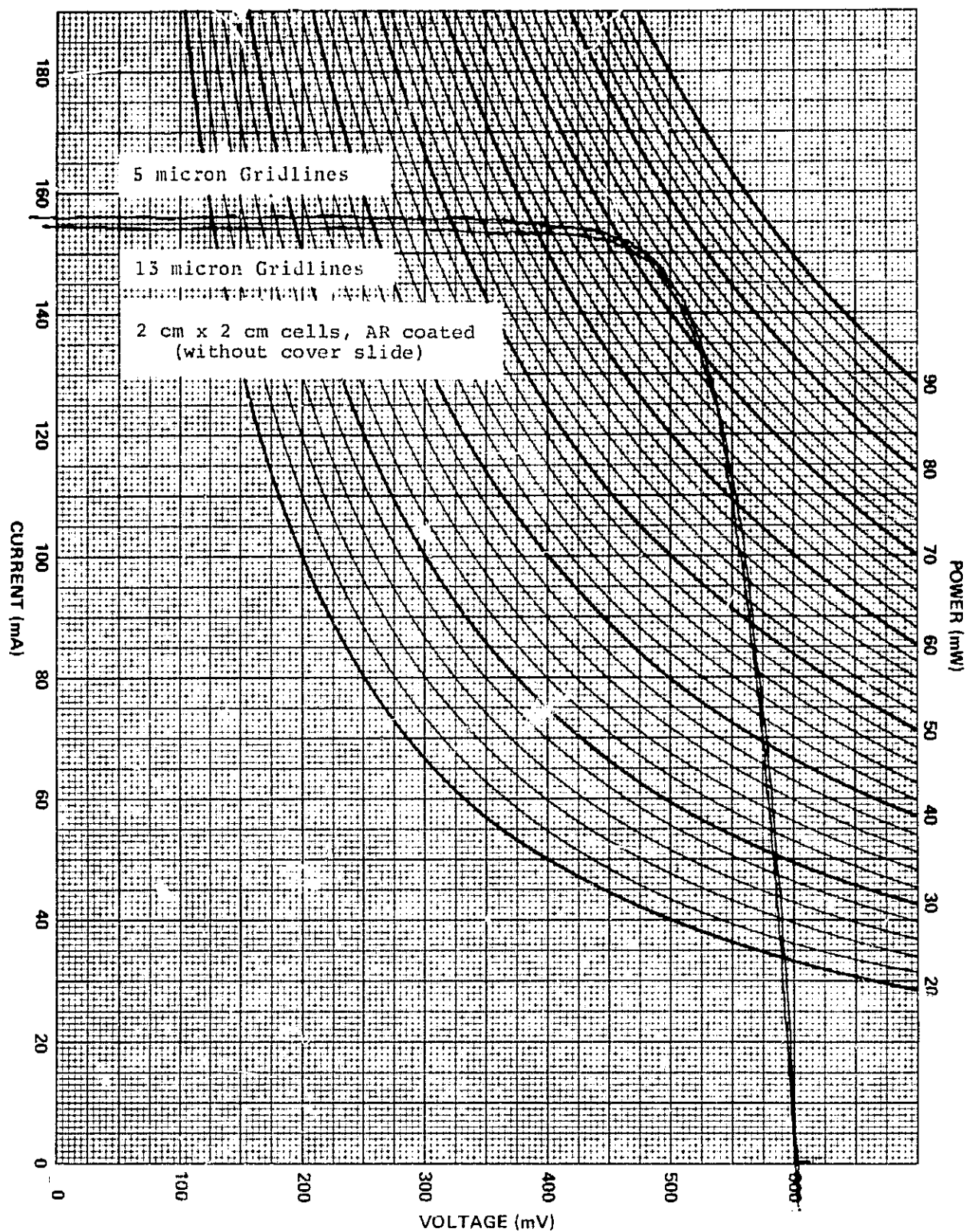


FIGURE 4. I-V CHARACTERISTICS FOR CO-PROCESSED CELLS WITH COARSE AND FINE GRIDLINES.

The means of coating evaluation consisted of reflectance measurements for films on silicon employing the Beckman DK-2A spectrophotometer. Also, observation of reflectance changes produced by overcoating the samples with silicone rubber cover-slide adhesive (medium optical index material) was used as a means to evaluate whether the anti-reflective coating's index would be high enough to provide the best optical match for cells finally assembled with cover slides. The as-deposited reflectance was measured as a function of incident light wavelength from 400nm to 1000nm and changes with post-deposition treatment and adhesive application were observed for evaluation of overall film optical properties.

The changes in evaporant source material consisted of:

- a) fresh Ta_2O_5 powder (Atomergic Chemetals Co.)
- b) Multiply vacuum-melted glass from the powder.
- c) Adding a back pressure of oxygen during evaporation in expectation of restoring stoichiometry after probable dissociation during evaporation.

The results of these experiments are shown in Figure 5, Figure 6 and Figure 7. These films were all electron-beam evaporated, with low starting background pressures. Fresh source charges of Ta_2O_5 powder produced curves of the type shown in Figure 5. The right-hand lower curve is the reflection obtained as deposited. The left-hand lower curve results after brief heating (seconds) at temperatures in excess of 350°C. The optical effect of the heating is to shorten the wavelength for quarter-wave

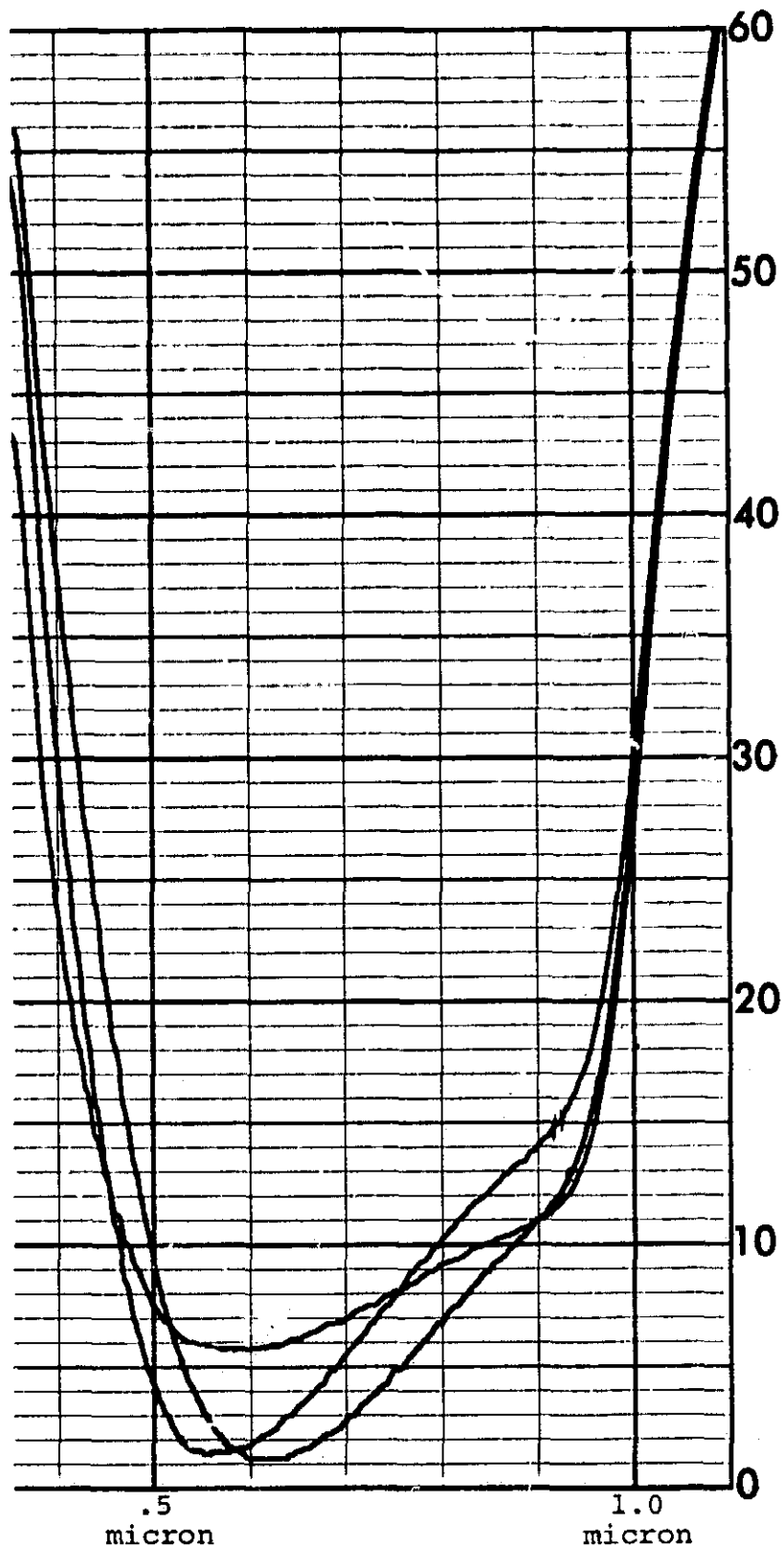


FIGURE 5. REFLECTION VS. WAVELENGTH - EVAPORATED FILM OF FRESH SOURCE Ta₂O₅ POWDER.

matching, most likely due to an index of refraction increase or physical shrinkage. Application of the silicone adhesive, which has a refractive index near 1.5, causes a net increase in reflectance across the silicon absorption band. This indicates a relatively low value of index of refraction for the film. These curves are very reproducible, always with an apparent film index too low for optimum optical matching of the adhesive layer and the silicon.

Figure 6 shows the set of reflectance curves measured when a background pressure of oxygen at 2×10^{-5} Torr is maintained during evaporation. Note that when the film is overcoated with the silicone, the reflectance is just slightly worse over the silicon absorption band, a somewhat surprising result.

Figure 7 shows typical reflectance curves for films produced by evaporating a tantalum oxide source which has been premelted in vacuum. These films show a higher reflectance before heating and not quite as low after heating as the previous film types. However, after coating with the silicone adhesive, there is a markedly lower reflectance over the silicon absorption band. Consequently, this evaporation technique was employed for all subsequent experimental cells fabricated, including those samples submitted to JPL.

Some attempts were also to be made to characterize the rate of film densification as a function of the temperature of post-deposition treatment. However, the densification takes only a few seconds, which is similar to the thermal time constant of the silicon itself, so that avenue was not pursued.

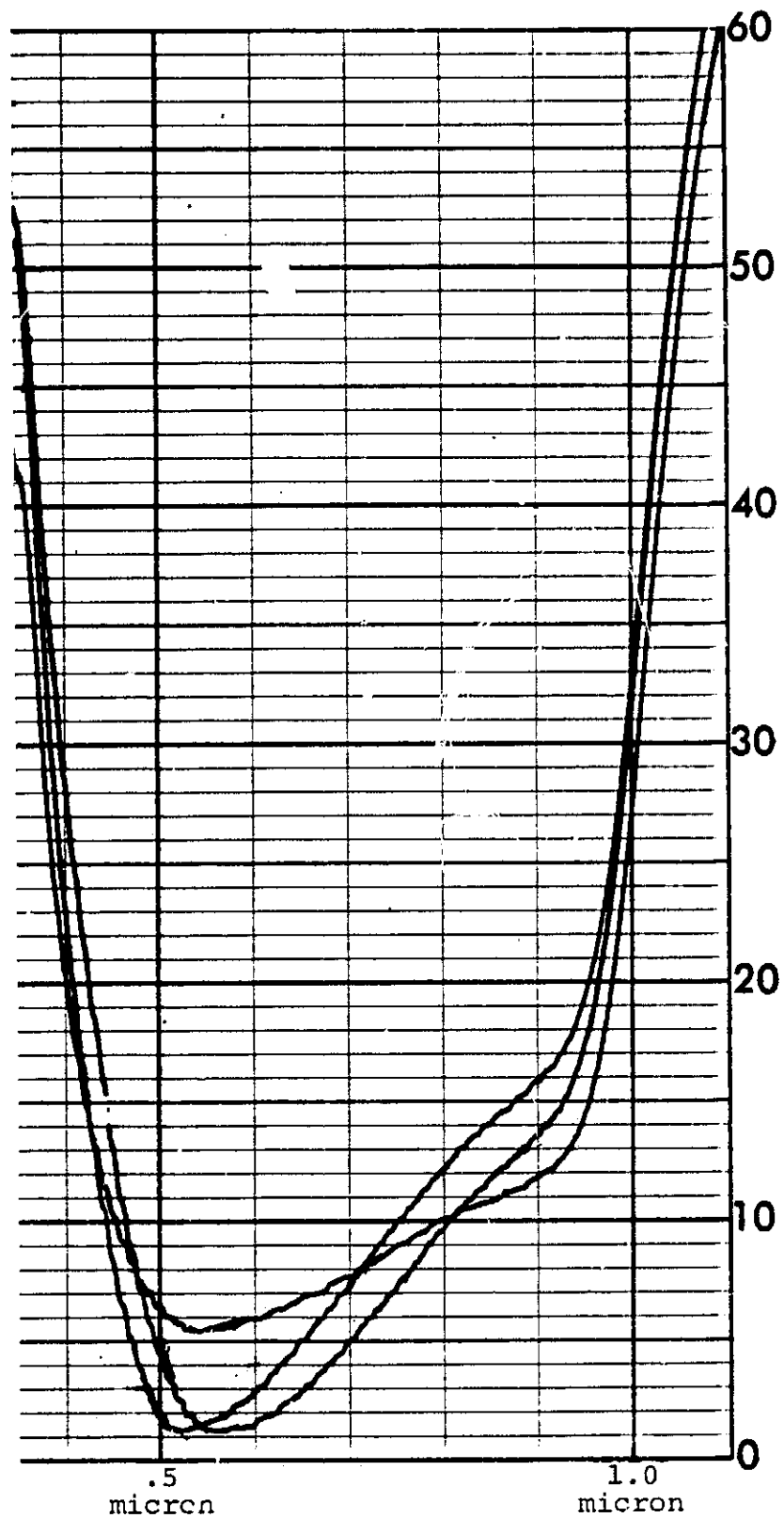


FIGURE 6. REFLECTION VS. WAVELENGTH - EVAPORATED FILM OF FRESH SOURCE Ta_2O_5 POWDER WITH O_2 BACK PRESSURE.

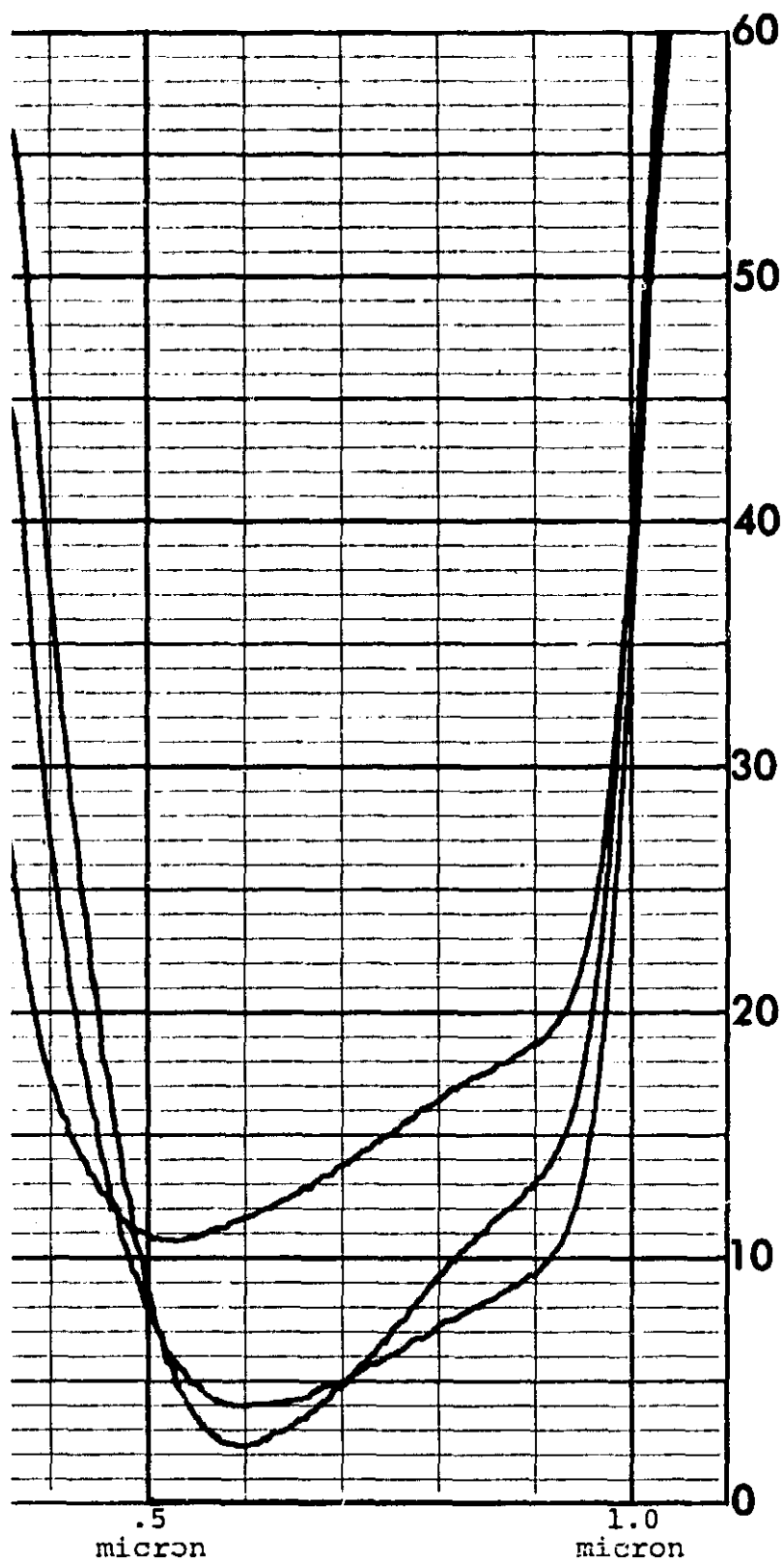


FIGURE 7. REFLECTION VS. WAVELENGTH - EVAPORATED FILM OF PRE-MELTED SOURCE Ta₂O₅ POWDER.

In summation, films made as those in Figure 7 have a refractive index high enough to produce an excellent optical coupling in the final embodiment with cover slide attached, adhesion has been found to be excellent (even on slightly contaminated silicon surfaces) and the material is also very resistant to hydrofluoric acid. Thickness control is relatively easy, by just observing the visible reflection passing purple, to match optimally at 600nm in the finished film after heat treatment.

D. Stability Testing

The first stability tests on representative experimental cells made in this contractual effort were performed in this quarter on a group of 2cm x 2cm cells representative of the fabrication techniques employed for the samples submitted to JPL.

The cells were first characterized under AM0 conditions with the Solarex xenon simulator and curve plotter. They were then subjected to a thermal soak at 150°C for 50 hours. After cooling, the cells were remeasured. There was no discernable change in either the I-V characteristics at AM0 or in physical properties (appearance, tape test) for any cell tested.

The cells were then put into liquid nitrogen until boiling ceased, rapidly transferred into boiling water and left for two minutes before being rapidly dunked back into the liquid nitrogen. This thermal cycle was performed at least five times for each cell.

Subsequent AMO measurement again showed no discernible change, nor did the physical properties.

E. Solar Cell Samples

During this quarter, a sample of one hundred 2cm x 2cm experimental solar cells were submitted to JPL for evaluation. These solar cells were diffused near the optimum conditions reported in the previous quarter, had the improved metallization pattern, were alloyed for approximately 60% back surface reflectance, and had high-index anti-reflective coatings applied from a pre-melted tantalum oxide source.

These solar cells were all measured on the Solarex xenon simulator prior to submission to JPL. They all displayed excellent fill factors, and blue response, and their thicknesses were varied from 120 microns to 260 microns.

V. CONCLUSION

- A. Rear-surface optical reflectance in the 50%-60% range is easily reproduced in the range of temperatures employed for alloying aluminum through the rear n^+ layer. Higher values would require major process changes.
- B. Anti-reflective coatings of tantalum oxide with the proper high refractive index to match silicon to the cover slide adhesive require use of a pre-melted evaporant source.
- C. The metallization pattern transmission is now limited by contact pad area and the lateral linewidth growth during metal thickening.
- D. Stability tests showed no observable degradation in cell properties.

VI. NEXT QUARTER ACTIVITIES

During the coming quarter, efforts on front surface texturing will accelerate, having been slowed by bottom face reflection studies within that task during the past quarter.

The tasks on handling techniques and production rate limiting steps for thin cells will commence in the coming quarter.

Front junction and p^+ formation will remain under continuous study, as will photovoltage improvement and interaction effects.

In addition, one hundred fifty (150) evaluation sample solar cells will be submitted to JPL during the coming quarter.